

(51) International Patent Classification ⁶ : C22B 3/18, B01J 8/00, 19/30	A1	(11) International Publication Number: WO 98/51828 (43) International Publication Date: 19 November 1998 (19.11.98)
(21) International Application Number: PCT/US98/09936 (22) International Filing Date: 15 May 1998 (15.05.98) (30) Priority Data: 60/046,639 16 May 1997 (16.05.97) US (71) Applicant: MBX SYSTEMS, INC [US/US]; 325 South Euclid Avenue, Tucson, AZ 85719 (US). (72) Inventors: SHARP, James, E. (deceased). STUFFLE, Kevin; 5775 South Old Spanish Trail, Tucson, AZ 85747 (US); KARLAGE, Kelly, L.; 1071 West Camino Desierto, Tucson, AZ 85704 (US). YOUNG, Tom, L.; 1438 West San Lucas Drive, Tucson, AZ 85704 (US). (74) Agents: SALIWANCHIK, David, R. et al.; Saliwanchik, Lloyd & Saliwanchik, Suite A-1, 2421 N.W. 41st Street, Gainesville, FL 32606-6669 (US).		(81) Designated States: AU, BR, CA, ID, MX, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

The diagram illustrates the BRC Conversion Cycle for Feedstocks to Fuels. The process begins with **Dry Copper Concentrates** entering a **Solvent Stripper**. **Refiner** and **Solvent** inputs are also shown. The output of the solvent stripper is **Kindge**, which goes to the **Rolling Down Mixing** stage. **Solvent Bio catalyst Polymer** is added to this stage. The output of the mixing stage is **BioBall Resyle**, which enters the **Rolling Down Wet Coating** stage. **BioBalls** are added here. The output is **Con Coated BioBalls**, which enters the **Rolling Down Dry Coating** stage. The output of the dry coating stage is **Raffinate**, which enters the **Raffinate Recycle** column. The output of the raffinate recycle column is **PLS**, which is pumped back to the **Solvent Stripper**. The **Raffinate Recycle** column also has a **Refiner** input. The **BRC Conversion Cycle Feedstocks to Fuels** section shows a **Leaching Vat** and a **Leaching Vat** (labeled as such in the diagram) with a **Leaching Vat** (labeled as such in the diagram) and a **Leaching Vat** (labeled as such in the diagram).

Process and bioreactor for enhancing the bioleaching of metals from sulfide mineral concentrations.

Startpunkt ist wieder
ausserliegend

DESCRIPTION

Chalcopyrite

SULFIDE MINERAL CONCENTRATE BIOLEACHING

5

Background of the Invention

10

Bioleaching of sulfide ores has been employed for many years in the extractive metallurgy industry. Successful bioleaching requires a thorough understanding of biological regimes and the role of each interrelating element therein. Enhancement of a bioleaching system requires not only a thorough knowledge of the interactive leaching elements, but also knowledge of tolerances for adjustments of those elements to effect the desired results. The goal of these processes is metal release or solubilization in an economically timely manner and concentration. Winning of the solubilized metal from a leach solution typically utilizes known extraction concentration technology such as Ion Exchange (IX) or Solvent Extraction (SX). Leach solutions thus concentrated are made amenable to standard precipitation technology such as crystallizers and/or electrowinning (EW) production of metal cathodes.

15

20

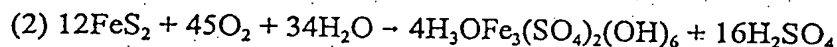
Some common bioleaching reactants in a sulfide leach system are: acidophilic *Thiobacillus ferrooxidans* and/or *Thiobacillus thiooxidans*; bacterial nutrients such as Med 64, Med 125, and PEGM, as disclosed in U.S. Patent No. 5,413,624; oxygen (air) and carbon dioxide; oxidizers such as ferric sulfate, ferric chloride and ferric methane sulfonate; acids such as sulfuric acid and hydrochloric acid; and reaction catalysts such as silver and carbonaceous materials including, but not limited to, graphite, natural or synthetic, activated carbon or petroleum coke. Temperature is interactive to the bioleaching system, either ambient or elevated by devices.

25

The chemistry of the bioleaching system is complicated by the proper or improper management of the stated reactants. Two sets of reactions caused by an enhancement of a particular reactant are as follows: oxygen enriched leaching of chalcopyrite (CuFeS_2) in the presence of a catalytic amount of silver as shown in U.S. Patent No. 3,856,913, as illustrated by the reactions

30

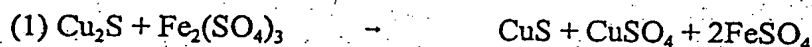
(1) $12\text{CuFeS}_2 + 51\text{O}_2 + 22\text{H}_2\text{O} \rightarrow 12\text{CuSO}_4 + 4\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 + 4\text{H}_2\text{SO}_4$
and if pyrite (FeS_2) is present with the chalcopyrite:



Both reactions generate sulfuric acid (H_2SO_4) which can lower the pH of the reacted solutions to an intolerable level for acidophilic bacteria which might have been present in the reactants, thus suppressing the contributions which might have been derived from the bacteria.

Conventional chalcocite (Cu_2S) and covellite (CuS) bioleaching reactions, which are enhanced only by the presence of a catalyzing inoculum, are as follows:

(*T.f.*) BAC



(*T.t.*) BAC



where *Thiobacillus ferrooxidans* serve to reoxidize the reduced ferrous sulfate (FeSO_4) to ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), while the *Thiobacillus thiooxidans* catalyze the continued solubilization of the reaction (1) product covellite (CuS).

A negative reaction product of chalcocite/covellite bioleaching is elemental sulfur (Reaction 2). The negative effect of sulfur is that it forms an amorphous layer over the remaining (non-leached) covellite (Wan, R.V. *et al.* [1984] "Electrochemical Features of the Ferric Sulfate Leaching of CuFeS_2/C Aggregates," Office of Naval Research, Fed. Rpt. No. 36). This amorphous layer is impenetrable to the catalyzing *T. thiooxidans*, which limits or eliminates further solubilization reactions.

The above stated reactions illustrate only two of the numerous leach conditions which must be understood and properly managed to effect a predictable and desirable result. Further concerns of leach management are materials handling of the leach components, both solid and liquids, such as sulfide mineral concentrate solids and sulfuric acid and/or acidified ferric sulfate liquid reactants.

The bulk solids fed to a particular reaction process must meet the economic constraints of the selected system. Low grade (low metal content) sulfide ores are typically bioleached in dumps or lined heap piles, whereas low grade sulfide concentrates must be processed in low cost reaction vessels, such as passive vat leach tanks or, for

higher grades, stir tanks or fluidized reaction vessels. Processing variables which further affect materials handling and processing costs are material feed size, whole ore or milled ore, metal content, solids retention time in reaction vessel (reaction rates), solid to liquid ratios, *i.e.*, slurry viscosities or pulp densities; and feed density, amenability of solids suspension (passive, stirring).

Recovery of metals from sulfide ores is often performed by first producing metal sulfide concentrates through flotation processes. Traditionally, the concentrates are smelted to drive off the sulfur and produce the metal. However, smelting is becoming environmentally unacceptable due to emissions of sulfur dioxide, and the quality of metals produced directly by smelting is inferior to that produced by leaching, solvent extraction, and electrowinning. Hence, there has been interest in processing concentrates by leaching, solvent extraction, and electrowinning.

Processes for refining of concentrates to the metal must meet economic constraints imposed by the marketplace. Stirred tank leaching of concentrates has several drawbacks, typically making it economically unviable. First, many concentrates are refractory to solubilization and require long residence times. Second, high power consumption is required for suspending and mixing of concentrates. In certain instances, stirred tank leaching of concentrates is performed under aggressive conditions using concentrated reagents and heating for higher value metals, but not for the base metals, such as copper and lead. Heap leaching of concentrates has also been investigated. However, processes for heap leaching of concentrates have encountered fluid flow problems such as channeling, ponding, and bypassing due to their fine particle size.

In areas of the world where there are few to no smelters, generally Western Europe, Africa, and parts of Asia, sulfuric acid is produced by burning sulfur. The plant needed to do this is capital-intensive. Operating costs are not much of a consideration due to the co-generation of electricity during the burning of sulfur which offsets the operating costs. A biological method to produce sulfuric acid solution from sulfur would be far less capital-intensive.

Brief Summary of the Invention

The subject invention pertains to processes for extraction of metals from sulfide mineral concentrates and for production of leaching reagents. In one embodiment, the processes of the subject invention utilize a substrate having a high external surface area. In a specific embodiment, this substrate is a ring and pin polyethylene packing, termed "BIOBALLS," to which the concentrates can be bound. The packing provides high external surface area per unit volume over which the concentrates can be thinly coated. The high density of the packing allows high pulp densities to be achieved while leaving a large pore space, which provides relatively uninhibited flow of leach process solutions.

In another embodiment, sulfur is thinly coated over substrates and bioleached to produce sulfuric acid, which can then be used as a reagent in metal leaching. In a specific embodiment, the bioleaching can be performed using *Thiobacillus thiooxidans*. The benefits of coating the sulfur onto "BIOBALLS" are the same as for the ores or concentrate, i.e., high exposed surface area and uninhibited flow of process solutions.

Packings can be used to mitigate the fluid flow problems encountered when heap leaching concentrates. Although crushed aggregate and crushed glass are examples of the packings that can be used, "BIOBALLS" offer much higher areal densities and leave more open space volume for fluid flow. Twenty percent pulp densities (w/w) are readily obtained with concentrates on "BIOBALLS."

Brief Description of the Drawings

Figure 1 is a schematic diagram of the metal-sulfide concentrate leaching process of the subject invention.

Figure 2 is a diagram of a stacked-segmented cell bioleaching column. Leach solutions are pumped to the top of the column and sprayed in Cell 1. The "BIOCAT" plus fungi inoculum-charged "BIOBALLS" provide a site for carbon dioxide generation and for degradation of organic entrained in raffinate. As the solutions pass through Cell 1, they dissolve carbon dioxide through a naturally aerated space between cells to trickle onto Cell 2. Cell 2 is charged with an inoculum-supporting substrate (sulfur for *T. thiooxidans* and pyrite for *T. ferrooxidans*) coated on the "BIOBALLS." As the leach solution passes through this Cell, ferrous ion is biooxidized to ferric, and the solutions

become charged with excess inoculum. The leach solutions then pass through Cells 3, 4, and 5, which are charged with concentrate-coated "BIOBALLS." Metal dissolution from the sulfide mineral concentrates generate a pregnant leach solution (PLS). The PLS is sent to an SX or IX plant for further processing.

5 Figure 3 diagrams a passive counter current vat bioleach system. "BIOBALLS" that are loaded with sulfide mineral concentrates have negative buoyancy, while "BIOBALLS" freed of their concentrate load float readily. Therefore, as the leach solutions solubilize the concentrate metals, the leached "BIOBALLS" can be decanted with the pregnant leach solution (PLS) and separated with a screen. The PLS is sent to
10 an SX or IX plant for processing, and the "BIOBALLS" are recycled to the concentrate loading plant for recoating.

Figure 4 is a diagram of "BIOBALL" concentrate heap leach and "BIOBALL" concentrate vat leach systems.

15 Figure 5 illustrates how the initial ferric iron concentration was varied to determine its effect on the extraction rate from 0 g/L to as high as 15 g/L.

Figure 6 is a general flow diagram for a biological method for producing sulfuric acid solutions from sulfur.

Detailed Disclosure of the Invention

20 The subject invention relates to those manageable portions of bioleaching, chemical leaching, materials handling methods, and processing devices, which when combined effect efficient methods for the commercial solubilization of metals from sulfide mineral concentrates. The sulfide mineral concentrate source material is generally produced by conventional froth flotation concentration. The mineral composition of
25 copper concentrates is generally a mixture of commercial metal sulfides combined with contaminate waste minerals such as pyrite and quartz, as well as by-product or co-product minerals such as silver, gold, and molybdenite. Concentrates of sufficient metal content are directly refined at primary smelters. Low-grade concentrates are either roasted and leached or mixed with high-grade concentrates to provide a commercial feed to a smelter.
30 The waste products from processing of sulfide concentrates by smelting or roasting are undesirable and environmentally damaging. Waste products such as sulfur dioxide

pollute air, arsenic and selenium residues pollute water, and leachates from slag piles pollute surface and ground water. Application of the methods, reagents, and devices which embody the subject invention can be used to commercially produce metals in a more environmentally responsible manner.

5 In a preferred embodiment, the subject invention provides materials and methods which allow for the enhanced bioleaching of finely ground sulfide mineral concentrates or sulfur. The concentrates or sulfur can be attached to high surface area substrates, such as "BIOBALLS," using a polymer binder formulation in a drum roll or other suitable operation. The coated and dried balls are placed in a vat, and leach solution is pumped
10 throughout the bed until the desired metal solubilization recovery is obtained, or in the case where sulfur is being leached, until the desired sulfuric acid production is obtained.

The oxidation potential of the leach solution can be enhanced for metal sulfide leaching by recycling through a biological ferric generator. The biological ferric generator is also referred to as a biological raffinate converter, or simply BRC. Many
15 sulfide minerals leach rapidly with high ferric solutions and the biological ferric generator is an economically efficient means of upgrading the ferric content of the reactant leach solutions.

In a specific embodiment of the subject invention, the reactor is a trickle bed type that uses a bed of catalyst/substrate-coated "BIOBALLS" that are inoculated with
20 *Thiobacillus ferrooxidans* bacteria which attach to the substrate and convert ferrous to ferric in the process solution as part of their metabolism. Conversion rates of about 0.8 g/L/h are routinely obtained in a 20 gallon laboratory reactor at iron concentrations up to 50 g/L. Once the desired level of leaching has been obtained, the leached balls are sent to a stripper where the tails are separated from the "BIOBALLS" and polymer. The
25 polymer and the balls are then recycled to the beginning of the circuit.

An additional aspect of the subject invention is an enhancement of blending a catalyst with the concentrates to enhance leach rate and recovery. A nutrient for iron oxidizing bacteria can also be incorporated. The combined catalyst and nutrient are referred to herein as "BIOCAT." In a preferred embodiment, the catalyst contains a
30 small percentage of graphite powder, which provides a site for elemental sulfur to crystallize, a common reaction product in sulfide mineral leaching (U.S. Patent No.

5,413,624). Further, the presence of graphite minimizes the blinding effects that can occur when the product sulfur forms an amorphous layer over the unleached sulfide minerals. The effect of graphite is to provide electrical conductance through the sulfur layer such that oxidation of the mineral can occur from oxidizing species in the process solution remotely. Graphite also provides a site for adsorption of oxygen in proximity to the mineral such that oxygen can oxidize subvalent cations (Fe^{2+} , for example) which subsequently oxidize the mineral. The nutrient medium provides a source of organic carbon and vitamins which support the growth and maintenance of oxidizing bacteria used in the leaching process. In one embodiment, the nutrient medium is PEGM, as is described in U.S. Patent No. 5,413,624.

A further aspect of the subject invention is the effective design of the reactors in which the concentrates are processed. Three basic reactor designs which can be utilized to bioleach sulfide mineral concentrates are exemplified herein. The reactor of choice is based on the following criteria:

1. Metal content of the concentrate measured in percent and subdivided for reference purposes as high or low grade.
2. Relative solubility of the concentrate in ferric sulfate, ferric chloride, or ferric sulfonate solutions.
3. Time requirements for commercial solubilization, *i.e.*, higher treatment costs demand short retention times, lower treatment costs allow for longer retention times.

To accommodate the above-stated concentrate processing requirements, the following reactor designs are described:

1. A passive countercurrent vat bioleach (Figure 3) with or without an ancillary biological ferric generator for ferric regeneration for low grade concentrates.
2. A passive segmented cell bioleaching column (Figure 2) wherein application leach solutions are spray applied to cells loaded with sulfide concentrates loaded on "BIOBALLS."
3. A passive heap or open vat leach (Figure 4) of stacked concentrate-loaded "BIOBALLS." Application leach solutions of ferric sulfate, or in the case

of sulfidic gold and silver concentrates a cyanide leach solution. The integration of a biological ferric generator would be optional.

5 The subject invention pertains to the bioleaching of sulfide mineral concentrates, ores, residues, and/or elemental sulfur. One aspect of the invention pertains to advantageous methods for producing sulfuric acid from sulfur. When elemental sulfur is contacted with an inoculum containing *Thiobacillus thiooxidans*, *Sulfolobus* or other oxidizing bacterial species, or other acidophilic microbes such as fungi in the presence of air and water, the sulfur is oxidized by these microorganisms to sulfuric acid which is contained in the resulting aqueous solution. After an equilibrium is established and the pH of the solution is lowered to 1 or less, a side stream can be removed and used directly or sent to reverse osmosis membrane units to be upgraded to a higher concentration of acid. Fresh water can be added as makeup for the volume of solution removed as a side stream. The process may be operated at ambient temperatures or at elevated temperatures depending upon the microorganisms used.

10 The sulfur may be coated onto "BIOBALLS" or may be used in granular form in columns or in heaps. The leaching of elemental sulfur to produce sulfuric acid is a non-polluting bio-process. It is applicable in all parts of the world with proper application and may be used with a minimal amount of equipment. Figure 6 shows schematically one embodiment of this process. This process facilitates the production of sulfuric acid without the use of expensive capital equipment and, if properly used, creates no pollution. Conversely, current technology utilizing the burning of elemental sulfur and the processing of the resulting gases containing sulfur dioxide through catalyst beds creates air pollution and requires enormous capital expenditures. Therefore, the process of the subject invention provides low cost sulfuric acid for mines and plants located in remote areas and in countries lacking the infrastructure necessary to handle the extremely dangerous concentrated sulfuric acid. Most leaching operations use aqueous solutions of sulfuric acid that contain less than 20 grams per liter of sulfuric acid. With current technology, sulfuric acid is made in very concentrated form and then shipped to the point of use where it is diluted with water to produce the aqueous solutions used in most leaching operations. Use of the process of the subject invention permits generation of

aqueous sulfuric acid solutions very near the point of use, eliminating the hazards to personnel and the environment that are associated with the current production of sulfuric acid. Pyrite may be substituted for elemental sulfur; however, an iron removal step may be required if upgrading of the acid is desired.

5 Experimental data demonstrate this process using *Thiobacillus thiooxidans*; however, any sulfur oxidizing acidophilic microorganisms may be used to produce sulfuric acid in the manner described herein. Sulfur may be present in any form that allows sufficient contact with oxygen and water.

10 The extraction of metals from sulfide concentrates or the production of sulfuric acid solution from elemental sulfur or pyrite is facilitated by the use of "BIOBALLS." However, said leaching of concentrates, ores, or residues occurs in the presence of carbon in solid form in agitated, stirred, or unstirred vats or tanks. The usage of the leached systems described herein are not limited to the use of columns of packed "BIOBALLS."

15 Materials and Methods

Chemical Leach:

Ferric sulfate. Chalcocite leach rate has long been known to increase in the presence of ferric ions. As the ferric ion oxidizes the copper, it becomes reduced to the ferrous ion. In the presence of oxygen and oxidizing bacteria such as *Thiobacillus*
20 *ferrooxidans*, it is converted back to ferric. This reaction occurs naturally as long as oxygen and bacteria are present. This same natural process can be accelerated through the use of a biological ferric generator.

Catalysts. Catalysts are utilized in many industrial processes. For bioleaching the catalyst called "BIOCAT" has been developed. "BIOCAT" is a mixture
25 of biological nutrients and finely ground graphite. The nutrient PEGM (U.S. Patent No. 5,413,624) can be used to provide a source of organic carbon and vitamins which support the growth and maintenance of the oxidizing bacteria used in leaching. The graphite component of "BIOCAT" provides a site for elemental sulfur, a common reaction product in sulfide mineral leaching to crystallize (Wan *et al.*, *supra*). Further, the
30 presence of the graphite minimizes the blinding effects that can occur when the product sulfur forms and amorphous layer over unleached sulfide minerals. The effect of the

graphite is to provide a site of conductance between the sulfide mineral and oxygen, thus providing continuance of the bacterially catalyzed leach reaction.

Materials Handling:

5 "BIOBALLS" have a skeletal ring and pin configuration which serves as a surface upon which substrate and sulfide mineral concentrates can be attached. Polyethylmethacrylate (PEMA), paraffin, and other comparable formulations can be used to attach sulfide mineral substrate to support *T. ferrooxidans* or *T. thiooxidans* inoculum. Paraffin and "BIOCAT" or concentrates have been coated onto "BIOBALLS" by dipping in molten paraffin and then dipping in "BIOCAT" or concentrates and cooling. PEMA and "BIOCAT" or concentrates have been coated onto "BIOBALLS" from solvent based slurries containing "BIOCAT" or concentrate and PEMA and drying. "BIOBALLS" can also be coated using crosslinkable aqueous polymer slurries such as furfural resins or PVA. Sulfur has been coated onto "BIOBALLS" by dipping "BIOBALLS" into the molten sulfur and then cooling. Utilizing the teachings provided herein, any binder system practiced in the art of coatings may be used.

15 Unloaded, plain HDPE "BIOBALLS" float while loaded "BIOBALLS" do not. Because of this, sulfide mineral concentrate-loaded "BIOBALLS" can be passively leached. By loading coated "BIOBALLS" into the bottom of a countercurrent vat leach system, "BIOBALLS" float to the surface of the vat when the sulfide mineral concentration is leached (Figure 3). Harvesting of the leached "BIOBALLS" which float to the surface can be accomplished by decantation of the leach liquor and screening of the "BIOBALLS." Recovered "BIOBALLS" can be recycled to coating drums, recoated with sulfide mineral concentrates, and reintroduced to the countercurrent vat leach system (Figure 3).

Reactor Design:

25 Two sulfide mineral concentrate bioleaching reactors were designed and tested. The two designs provide different economics for extraction of different grades and types of sulfide mineral concentrates.

30 The first design is a passive countercurrent flooded vat bioleaching system (Figure 3). The countercurrent system is most useful for chemical leaching with sulfuric or MSA ferric solutions. The countercurrent system also allows extraction of acid

leached "BIOBALLS," which float to the surface of the tank and decant with the PLS. A second design is a percolated stacked-segmented cell bioleaching column designed to process refractory sulfide mineral concentrates or to bioleach sulfur to produce sulfuric acid. The reactor design provides continuous inoculation and aeration of the concentrate loaded in "BIOBALL" cells (Figure 2). The design anticipates that the sulfide mineral concentrates are of a grade that a medium- to long-term residence will not adversely affect economics. The reactor is passive air side, requiring only solution pumping, with no gas injection or moving parts.

A schematic diagram of a sulfuric acid production process is shown in Figure 6. Sulfur and nutrient can be coated onto an appropriate substrate such as "BIOBALLS" and reacted with water in a bioreactor (shown in Figure 2) and catalyzed with *Thiobacillus thiooxidans* inoculum. The reactor would produce a sulfuric acid solution of pH 2 or less. If more concentrated acid is needed, ion exchange or reverse osmosis technology can be used.

Following is an example which illustrates a procedure for practicing the invention. This example should not be construed as limiting. All percentages are by weight and all solvent mixture proportions are by volume unless otherwise noted.

Example 1 — Leaching of Low-Grade Copper Concentrates Using "BIOBALLS"

"BIOBALL" packing was used as a substrate for low-grade (considered too low-grade for direct smelting but contains significant metal value) copper concentrates from a mine in Arizona. Two tests were conducted in parallel. In one test, concentrates were used alone. In the other test, concentrates were combined with "BIOCAT." The low-grade copper concentrates were leached with biologically-generated high ferric lixiviant in shaken vats. The initial ferric iron concentration was varied to determine its effect on the extraction rate from 0 g/L to as high as 15 g/L (Figure 5).

Copper concentrates were loaded onto "BIOBALLS" using the following procedure. Two batches of 250 g of dried concentrates were weighed. One batch was blended with a "BIOCAT" amendment of 5% by weight. Binder (medium molecular weight polyethylmethacrylamide) was added from a concentrated solution in acetone at

13 percent by volume of total solids. Additional acetone was added to reduce the viscosity of the slurry until pourable. One inch diameter "BIOBALLS" were then dipped into the slurry, rolled in a bed of dry concentrates, and dried. Twenty coated balls of each were prepared. Each batch of coated "BIOBALLS" was placed in a one-gallon polyethylene jar. 1200 ml of leach solution was added to each jar, which was sufficient to just cover the loaded "BIOBALLS." The leach solutions consisted of sulfuric acid at 10 g/L and additions of biologically generated ferric sulfate. The ferric content was varied in individual leach cycles to assess the effect of ferric concentration. Individual leach cycles were typically two days, but were increased in duration toward the end of the leach. The leach period was 30 days. The results of this experiment are summarized in Table 1. Ninety-three percent of the acid soluble copper was extracted without addition of "BIOCAT." Ninety-eight percent of the acid soluble copper was extracted with the addition of "BIOCAT."

Table 1. Ferric sulfate leach of chalcocite concentrates					
<i>Concentrates without catalyst</i>					
Day	Leach cycle	Copper (g/L)	<i>T. ferrooxidans</i> (g/L)	% extracted per leach	Cumulative % Cu extraction
1	1	2.00	2.2		
2		5.40	3.0	8.00%	8.00%
3	2	8.50	10.0		8.00%
4		8.50	9.5	12.50%	20.50%
5	3	6.00	8.8		20.50%
6		6.80	9.2	16.00%	36.50%
7	4	6.50	15.9		36.50%
8		8.60	16.8		36.50%
9		9.30	15.5	16.50%	53.00%
10	5	2.00	2.9		53.00%
11		2.20	2.9	3.90%	56.90%
12	6	1.17	1.5		56.90%
13		1.65	1.5	2.90%	59.80%
14	7	2.80	9.6		59.80%
15		4.00	8.9		59.80%
17		7.40	11.3	13.10%	72.90%
19	8	2.80	4.3	5.00%	77.90%
21	9	3.40	14.7		77.90%
32		8.90	15.3	15.70%	93.60%
TOTAL:					93.60%

<i>Concentrates with biocatalyst</i>					
Day	Leach cycle	Copper (g/L)	<i>T. ferrooxidans</i> (g/L)	% extracted per leach	Cumulative % Cu extraction
1	1	2.30	2.2		
2		5.70	3.2	12.10%	12.10%
3	2	7.50	9.6		12.10%
4		8.60	10.0	18.30%	30.40%
5	3	3.40	5.9		30.40%
6		5.90	8.8	20.10%	50.50%
7	4	3.70	16.1		50.50%
8		5.70	16.8		50.50%
9		6.10	16.2	15.60%	66.10%
10	5	1.56	2.5		66.10%
11		1.84	2.6	4.70%	70.80%
12	6	1.07	1.4		70.80%
13		1.46	1.5	3.70%	74.50%
14	7	1.56	9.5		74.50%
15		2.20	9.6		74.50%
17		4.50	12.0	11.50%	86.00%
19	8	1.50	4.5	3.80%	89.80%
21	9	1.20	15.1		89.80%
32		3.40	15.5	8.70%	98.50%
TOTAL:					98.50%

The results of the leach study verify the applicability of the subject invention for extraction of metals from concentrates and demonstrate the benefit of the additions of "BIOCAT."

Example 2

A column containing sulfur packed onto "BIOBALLS" was treated with an inoculum containing *Thiobacillus thiooxidans*. The initial aqueous solution used to start the inoculum had a pH of 6. Three days later, the pH of the solution had decreased to

1.73. These data demonstrate by the lowering of the pH that sulfuric acid is being generated by the *Thiobacillus thiooxidans*.

5 It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims.

Claims

1 1. A process for extraction of metals from sulfide mineral concentrates or for the
2 production of sulfuric acid from sulfur which comprises

3 (a) binding said concentrates or sulfur to high areal density packing to obtain
4 high pulp densities and a high fraction of open volume for flow of process
5 solutions; and

6 (b) leaching said metals or said sulfur.

1 2. The process, according to claim 1, wherein the high areal density packing is
2 a sphere that is comprised of a ring and pin arrangement.

1 3. The process, according to claim 2, where the packing is made from
2 polyethylene or any recyclable material.

1 4. The process, according to claim 1, wherein graphite or graphite and a nutrient
2 are blended with the sulfide mineral concentrates prior to being bonded to the packing.

1 5. The process, according to claim 1, wherein the leach solution is amended with
2 ferric sulfate.

1 6. The process, according to claim 1, wherein the binding agent is a polymer.

1 7. The process, according to claim 6, wherein the polymer is
2 polyethylmethacrylate.

1 8. The process, according to claim 1, wherein said packing is coated with a
2 biological nutrient and catalyst to support the health and growth of acidophilic microbes.

1 9. The process, according to claim 8, wherein said acidophilic microbe is selected
2 from the group consisting of *Thiobacillus thiooxidans*, *Thiobacillus ferrooxidans*, and
3 fungi.

1 10. A biological reactor for enhanced concentrate leaching which comprises a
2 column of stacked bioreactor cells comprising:

- 3 (a) a cell wherein oxidizing bacteria are provided a substrate that is coated on
4 "BIOBALLS" which supports and sustains their activity;
5 (b) a leaching cell where concentrate-loaded "BIOBALLS" are leached;
6 (c) a design of stacked cells which provides maximum natural air flow
7 through the segmented cells; and
8 (d) a double lined leach cell which assures maximum air flow past the entire
9 stack of "BIOBALLS" in the cell.

1 11. A countercurrent vat leaching system wherein the differential density of
2 loaded versus leached "BIOBALLS" allows loaded balls injected into the bottom of the
3 vat to slowly rise as the concentrate load is leached away.

FIG. 1

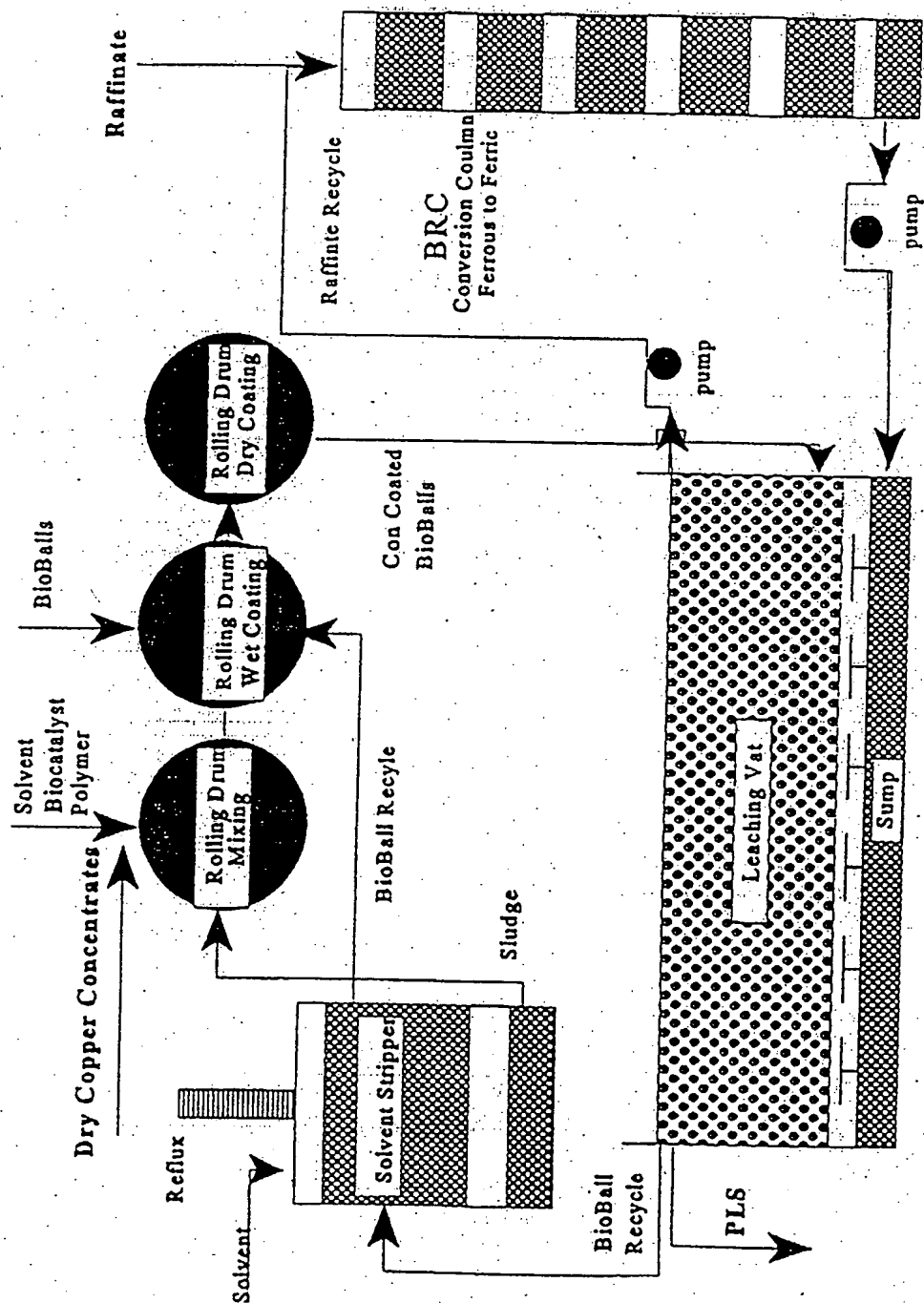
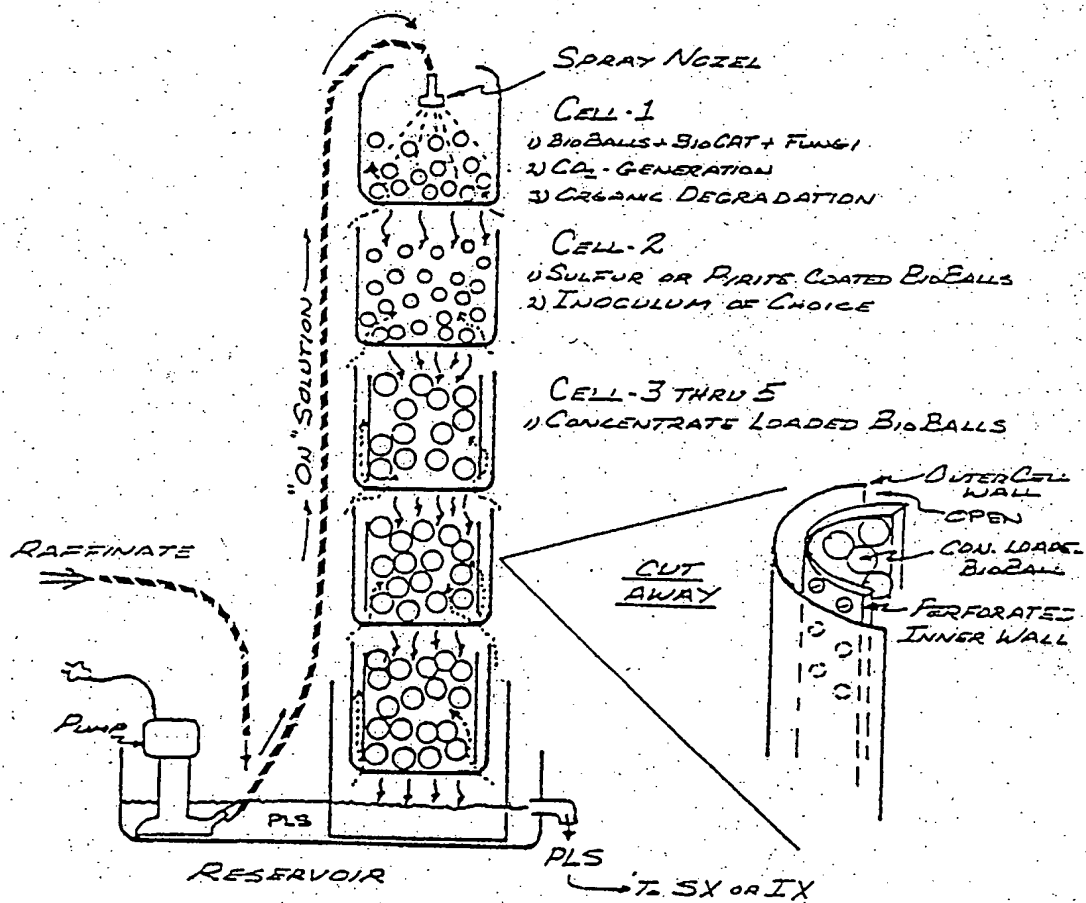


FIG. 2



EXPLANATION

Drawing Not to Scale.

--- Airflow Lines - Natural Convection

— Solution Flow Lines

SX - External Solvent Extraction Plant

IX - External Ion Exchange Plant

— Raffinate "On" Solution From SX or IX Plant

PLS - Pregnant Leach Solution

FIG. 3A

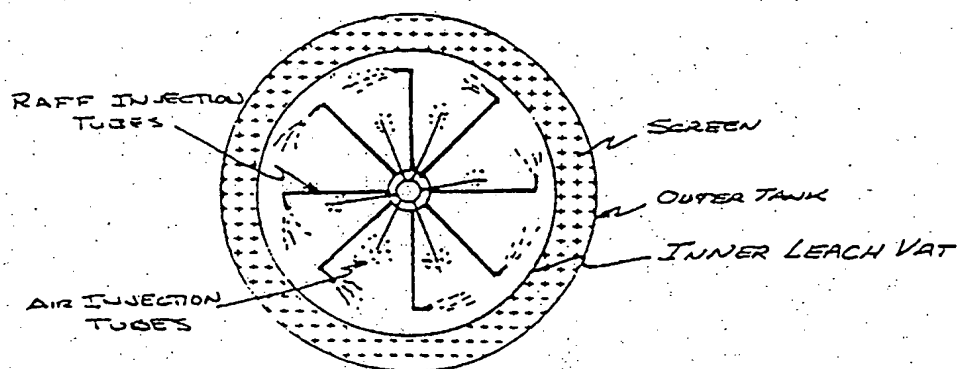
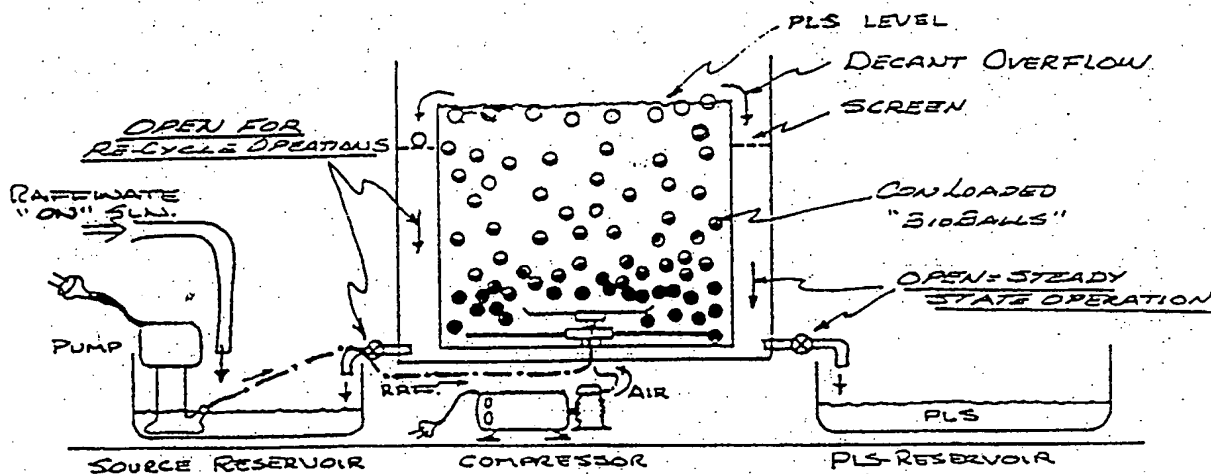


FIG. 3B



EXPLANATION

Drawing Not to Scale

- Fully LEACHED BioBall
- ◐ Partially LEACHED BioBall
- Fully Concentrate LOADED BioBall

FIG. 4A

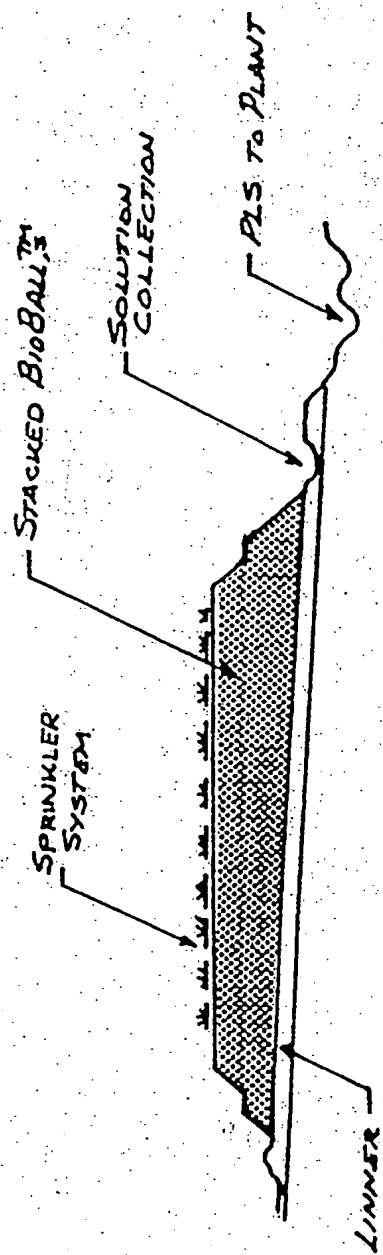


FIG. 4B

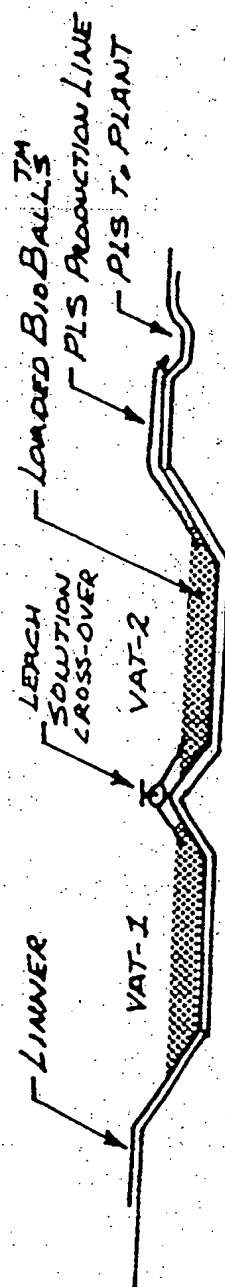


FIG. 5

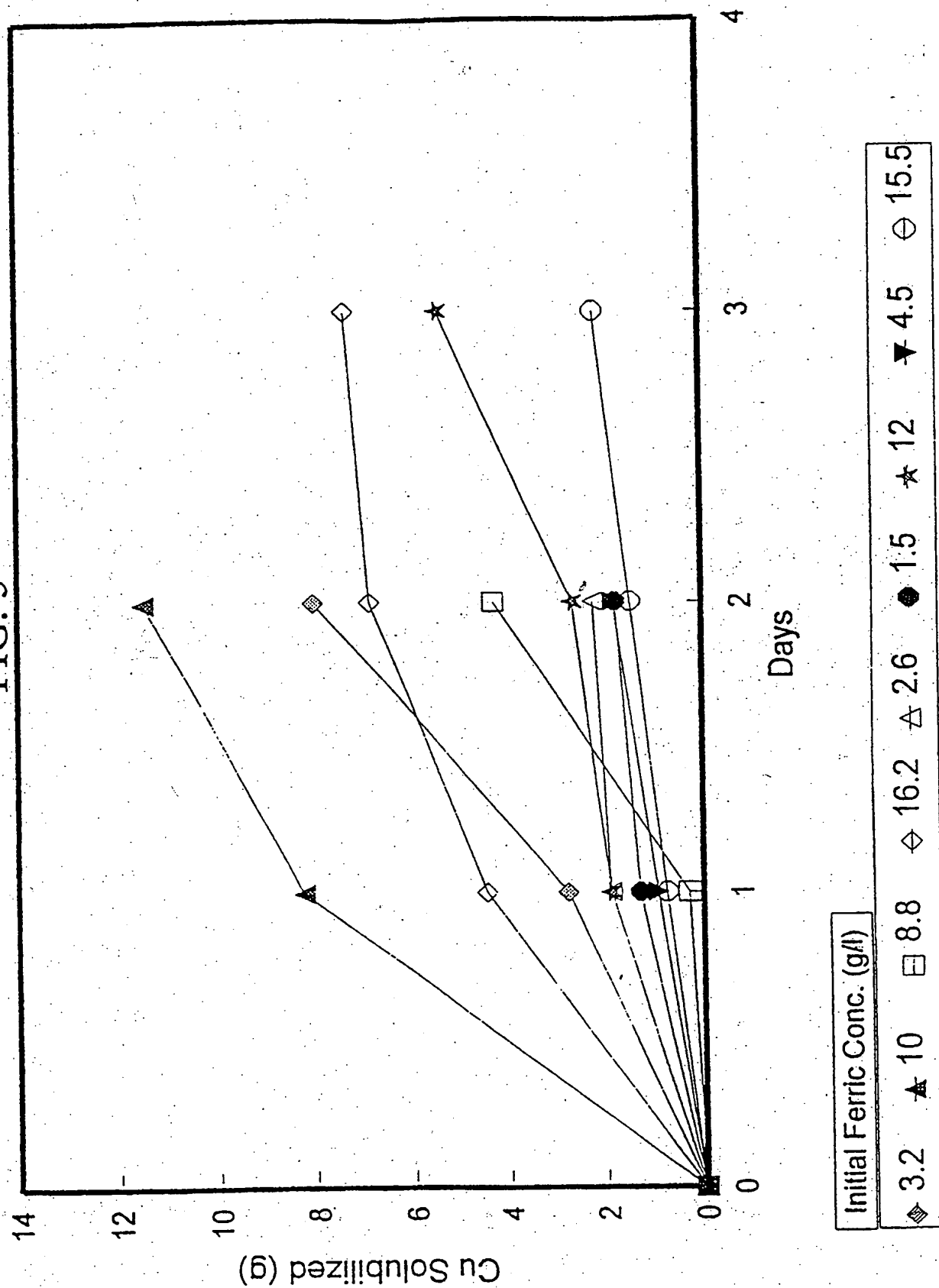
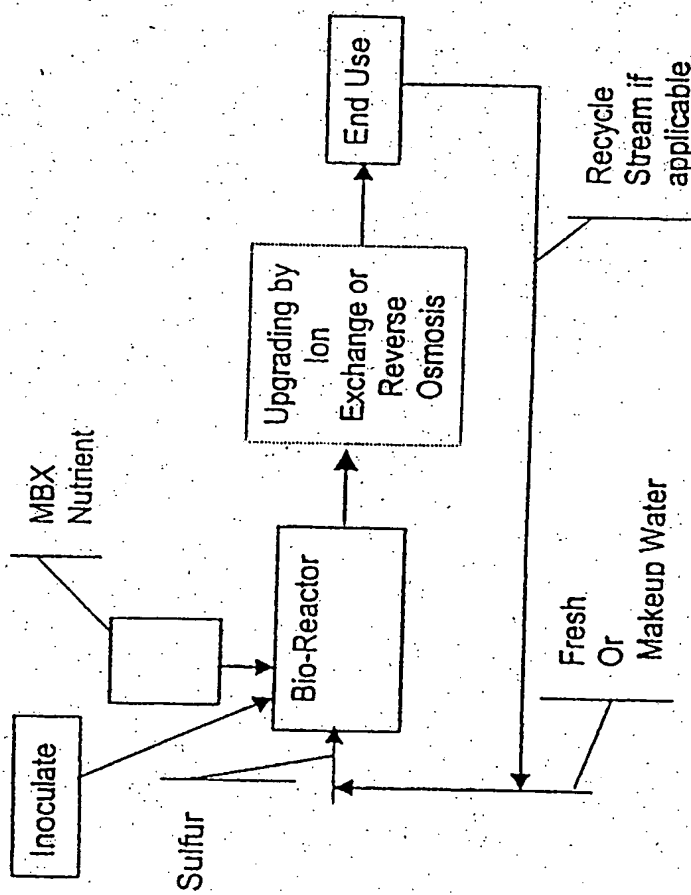


FIG. 6



INTERNATIONAL SEARCH REPORT

National Application No.

PCT/US 98/09936

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C22B3/18 B01J8/00 B01J19/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C22B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	DATABASE WPI Section Ch, Week 9834 Derwent Publications Ltd., London, GB; Class A88, AN 98-388663 XP002077560 & CA 2 186 202 A (ALBERTA ENVIRONMENTAL CENT), 24 March 1998 see abstract	1, 2, 6, 8, 10
X	GB 2 225 256 A (TOLMIN MINERAL TECHNOLOGIES NV) 30 May 1990 see claims 1-7	1
A	WO 89 05688 A (ENVICON LUFT & WASSESTECHNIK) 29 June 1989 see example 1	2, 3
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents:**

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

15 September 1998

Date of mailing of the international search report

30/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Kesten, W

INTERNATIONAL SEARCH REPORT

national Application No
PCT/US 98/09936

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT.

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 8108 Derwent Publications Ltd., London, GB; Class L02, AN 81-12929D XP002077561 & JP 55.162490 A (SUMITOMO ALUMINIUM SMELTING CO), 17 December 1980 see abstract</p>	1
A	<p>US 3 856 913 A (MCELROY R ET AL) 24 December 1974 cited in the application see claims 1-13</p>	1-9
A	<p>US 5 413 624 A (SHARP JAMES E ET AL) 9 May 1995 cited in the application see claim 1</p>	1-9
A	<p>WAN, R. Y. ET AL.: "Electrochemical Features of the Ferric Sulfate Leaching of CuFeS₂/C Aggregates" OFFICE OF NAVAL RESEARCH, TECHNICAL REPORT NO. 36, 28 November 1984; XP002077559 cited in the application</p>	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/09936

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2225256 A	30-05-1990	AU 630889 B	12-11-1992
		AU 4262989 A	12-04-1990
		US 5021069 A	04-06-1991
WO 8905688 A	29-06-1989	EP 0354209 A	14-02-1990
US 3856913 A	24-12-1974	CA 968955 A	10-06-1975
		SE 375114 B	07-04-1975
US 5413624 A	09-05-1995	US 5248329 A	28-09-1993
		US 5221327 A	22-06-1993
		AU 654544 B	10-11-1994
		AU 1583992 A	15-09-1992
		JP 6506503 T	21-07-1994
		WO 9214848 A	03-09-1992
		US 5283192 A	01-02-1994